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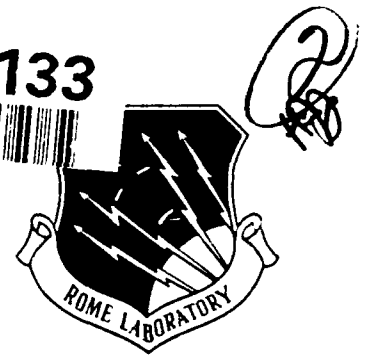

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ORGANIC POLYMERIC ELECTRO-OPTIC MATERIALS: SYNTHESIS, PROCESSING AND DEVICE APPLICATIONS

University of Massachusetts

Jayant Kumar and Sukant Tripathy

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13. ABSTRACT (Maximum 200 words)

A number of polymeric second and third order nonlinear optical materials were designed and synthesized. The materials were characterized for their thermal properties and processed into thin films by Langmuir-Blodgett technique or spin coating methods which then were evaluated by second harmonic generation and electric field induced phase changes by interferometery. Stable second order nonlinear coefficient was obtained in crosslinked systems. Waveguiding with low loss was achieved in spin coated nonlinear optical polymer films, and frequency doubling experiments in waveguide configuration were performed.

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Organic Polymeric Electrooptic Materials:
Synthesis, Processing and Device Applications

This document is the final report on the contract "Organic Polymeric Electro-optic Materials": Synthesis, Processing and Device Applications (contract number F19628-88-K-0048)

The objectives of the proposed research as outlined in the proposal were:

1. Identification and design of organic materials exhibiting high second order and third order nonlinear susceptibility.

2. Synthesis and purification of selected organic compounds and polymers showing promise of enhanced optical nonlinearity.

3. Characterization and processing of compounds synthesized.

4. Measurement of linear and nonlinear optical properties of thin films.

5. Electro-optic measurements, waveguiding, and device considerations.

1. Identification and design of organic materials exhibiting high second order and third order nonlinear optical (NLO) susceptibility.

Molecules with strong donor-acceptor groups bridged by π -delocalized moiety are noncentrosymmetric and give rise to large second order hyperpolarizability, β. The intramolecular charge transfer in such molecules greatly enhances the hyperpolarizability[1-3], β. In addition to the large values of β, such molecules also posses large values of third order hyperpolarizability, γ because they have extended planar structures. By incorporating large densities of such chromophores in a polymer, relatively large values of bulk second and third order nonlinear optical susceptibilities, $\chi^{(2)}$ and $\chi^{(3)}$ are possible. Incorporation of some of these dyes as sidegroups into π-delocalized polymers such as polydiacetylenes can lead to very large values of third order NLO susceptibility $\chi^{(3)}$. The structures of some of the representative molecules to be synthesized are

shown in Figure 1. The cut-off wavelength of these molecules are at relatively short wavelengths compared with traditional azo and stilbene compounds. Apart from synthesis of the dyes, considerable synthetic effort is also required to modify the polymers and the dyes so that they form a crosslinkable polymer system with a high glass transition temperature, T_g. For Langmuir-Blodgett (LB) film studies the dyes and polymers were functionalized with hydrophobic and hydrophilic groups to form monolayers and multilayers on appropriate substrates.

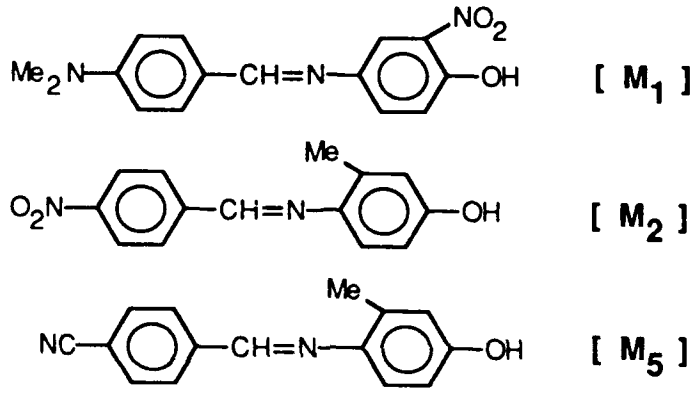

Figure 1. Molecular Structures of Some Representative Molecules.

Molecular units which have large second order and NLO hyperpolarizabilities are necessary to yield large macroscopic nonlinearities. Using the readily available quantum chemistry software at U-Lowell molecular modelling laboratory it was concluded that for second order hyperpolarizability an NLO moiety or chromophore should satisfy the following criteria:

a) delocalized moiety (including π -extended systems such as stilbene, azo, azomethine and others).

b) electron-donating group (linked through oxygen and nitrogen atoms, for example).

c) electron-withdrawing group (e.g., nitro, cyano).

d) Functionality which can form cross-links or polymerize upon heating or exposure to UV or make the molecule surface active.

e) wavelength tunability.

2. Synthesis and purification of selected organic compounds and polymers showing promise of enhanced optical nonlinearity

The nonlinear optical chromophores selected on the basis of molecular design considerations were azomethine dyes with different donor acceptor groups. The azomethines can be synthesized by a one step coupling reaction with large yields. Figure 2 part-1 shows the reaction scheme for the synthesis of one of the dyes which we denote M_1. Part-II of Figure 2 shows the synthesis scheme for covalently incorporating the NLO chromophore M_1 into polymethacrylate backbone. The spacer of the pendant group containing the dye can be varied as desired. Part-III of Figure 2 also shows the synthetic scheme for preparing diacetylene monomers as well as polymers incorporating the NLO chromophore M_1. The surfactive diacetylene polymer may be used to assemble LB films which can show large second and third order NLO properties.

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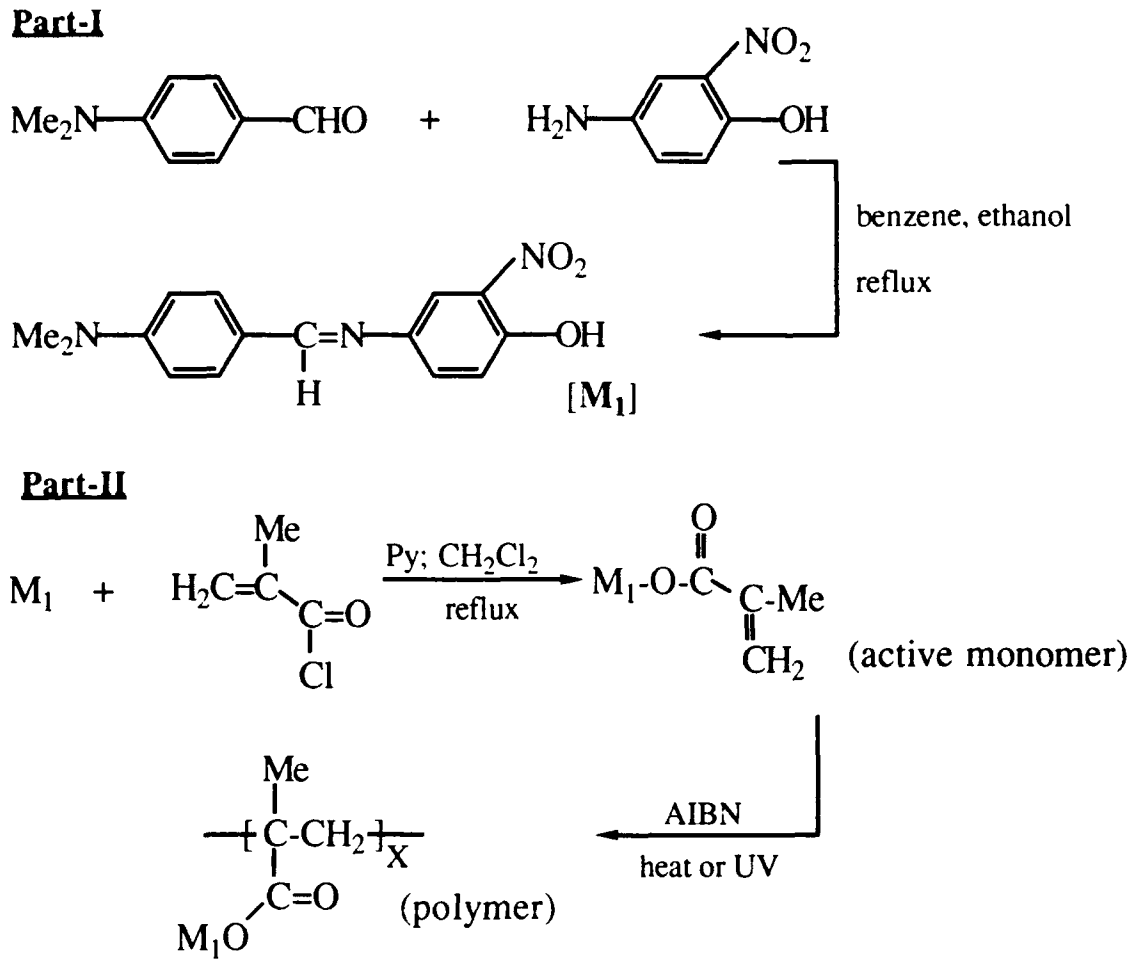
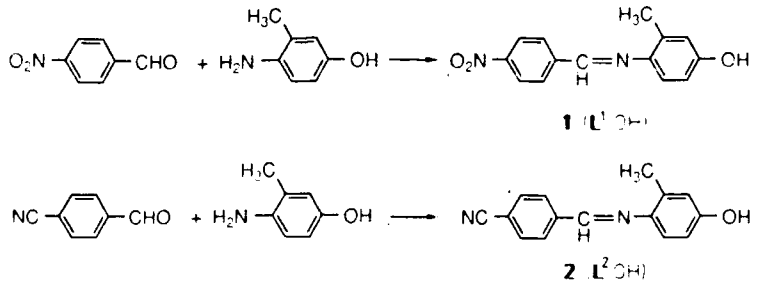


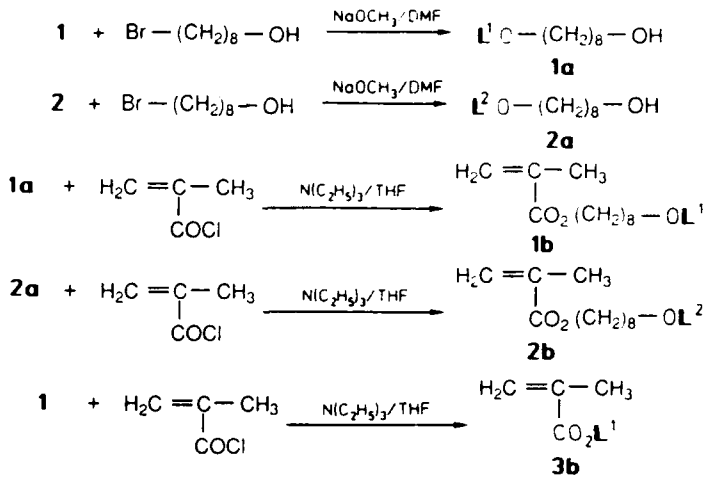
Figure 2. Synthetic Scheme Showing Representative Reactions.

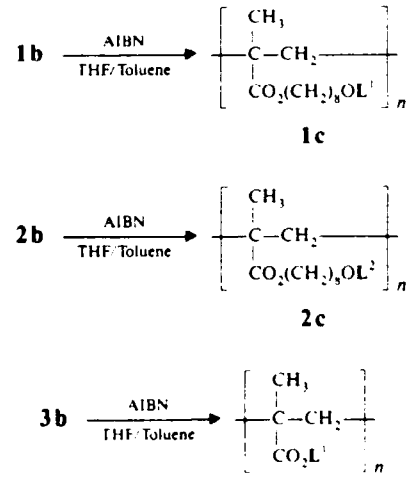
Scheme 1 outlines the synthesis of a number of polymethacrylate based polymers containing NLO active pendant sidegroups. The NLO moieties in all these polymers are azomethine dyes. Monomers were polymerized by free radical polymerization to yield the homopolymers shown. Copolymers were synthesized by copolymerization with methyl methacrylate (MMA), using 5:1 and 18:1 mole ratios, respectively. High molecular weight product is obtained as the proportion of MMA is increased. The products were purified by column chromatography techniques or precipitating the soluble polymer out of solution. The details of the synthetic scheme, yields and purification have been discussed by Mandal[4] et al.

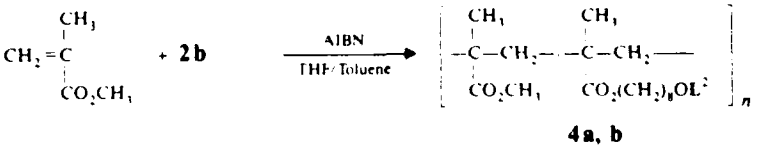
Our approach to cross-linked systems[5] is based on thermal crosslinking or photocrosslinking leading to high T_g systems. We give an example of a photocrosslinkable second order NLO polymer developed at ULowell which is quite stable for long periods of time. It involves essentially one or more photosensitive chromophores (namely, cinnamoyl group) in both the host polymer and the active dye molecule. The active dye molecule in this case is an azo dye which is functionalized with the cinnamoyl group. These chromophores undergo intermolecular photocross-linking reaction (as observed in polyvinylcinnamate) subsequent to poling of the active molecules doped in to the photosensitive polymer matrix. Investigations have been carried out using polyvinylcinnamate (PVCN) as the model host polymer and an extended π-conjugated azo dye system appropriately substituted with donor, acceptor and cinnamoyl groups as typical NLO molecules. The NLO units have also been incorporated covalently into the photocrosslinkable polymers.

Scheme 1:


O2N
CHO
+ H2N
H3C
OH
C=N
H
1 (L1OH)
NC
2 (L2OH)


1 + Br—(CH2)8—OH
NaOCH3/DMF
L1O—(CH2)8—OH
1a
2 + Br—(CH2)8—OH
NaOCH3/DMF
L2O—(CH2)8—OH
2a
1a + H2C=C(COCl)—CH3
N(C2H5)3/THF
H2C=C(CH3)—CO2(CH2)8—OL1
1b
2a + H2C=C(COCl)—CH3
N(C2H5)3/THF
H2C=C(CH3)—CO2(CH2)8—OL2
2b
1 + H2C=C(COCl)—CH3
N(C2H5)3/THF
H2C=C(CH3)—CO2L1
3b


1b
AIBN
THF/Toluene
CH3
C—CH2
CO2(CH2)8OL1
n
1c
2b
AIBN
THF/Toluene
CH3
C—CH2
CO2(CH2)8OL2
n
2c
3b
AIBN
THF/Toluene
CH3
C—CH2
CO2L1
n
3c


CH2=C(CH3)—CO2CH3
+ 2b
AIBN
THF/Toluene
CH3
C—CH2
CO2CH3
CO2(CH2)8OL2
n
4a, b

Diazo-linked extended systems have been synthesized[5] by diazo coupling reaction of aromatic molecules appropriately substituted with donor-acceptor groups and hydroxyl groups. Nitro- and N,N-diethylamine are chosen as acceptor and donor groups, respectively, and placed at either end of the extended molecule in order to obtain large second order electro-optic effects. Likewise, one hydroxyl group in each aromatic ring is appropriately substituted for coupling with a photosensitive chromophore. Figure 3 shows the structure of one of the photocrosslinkable nonlinear optical polymers -- PVCN (polyvinylcinnamate)/CNNB-R (3-cinnamoyloxy-4-[4-(N,N-diethylamino)-2-cinnamoyloxy phenylazo] nitrobenzene) .

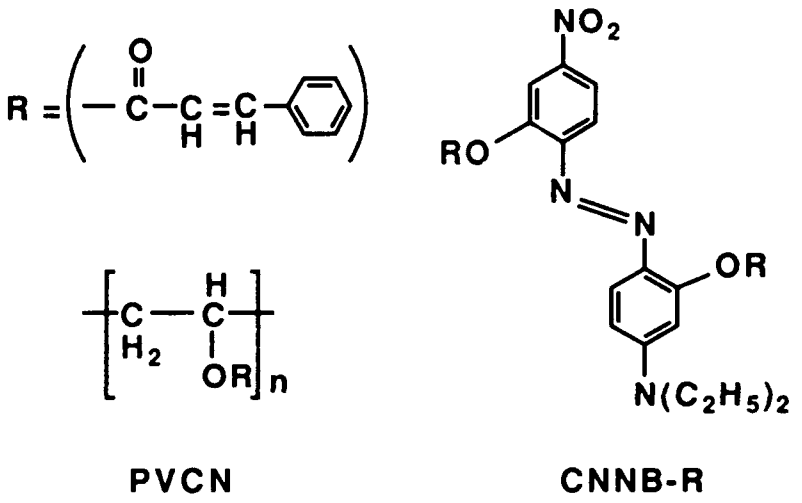


Figure 3. Structures of the Photocrosslinkable Pair CNNB-R (NLO Chromophore) and the Polymer PVCN for the Cross-linked NLO Polymer.

A wide range of chromophores are available for crosslinking purposes. The classic example of photocross-linking by an excited chromophore occurs in PVCN. Cross-links are formed by 2 + 2 photodimerization between an excited cinnamoyl group of one chain with a ground state cinnamoyl group belonging to another or the same chain. The photodimerization between two C=C double bonds of cinnamoyl groups is very effective because of the adjacent carbonyl group which provides desirable polarization towards the reactivity of the double bond. The phenyl group, on the other hand, increases the polarizability and the absorption coefficient of the chromophore. The intermolecular photocross-linking reaction between the photosensitive chromophores of the polymer and the active molecules is represented in Figure 4.

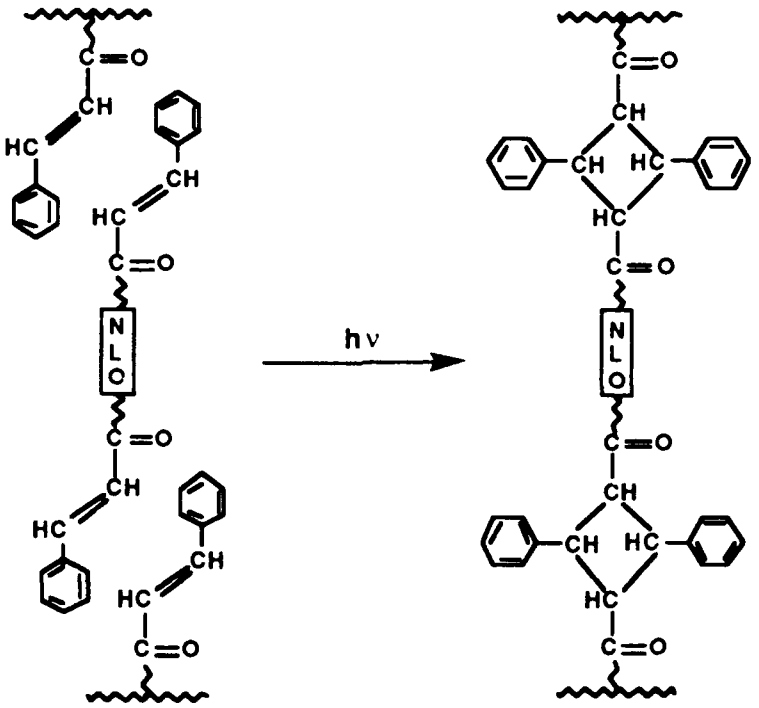


Figure 4. Photocrosslinking Reaction Functionalized NLO Dye and PVCN.

Poling and photocrosslinking the PVCN/CNNBR system leads to large second order nonlinearity (d_{33}~20 pm/V) which is stable at room temperature. The details are given in a paper by Mandal[6] et al.

3. Characterization and processing of NLO materials.

The NLO dyes and polymers synthesized were characterized for their optical properties by UV-Visible spectroscopy. The dipole moments were estimated using quantum chemical calculations and the second order hyperpolarizability was evaluated by solvatochromic shifts of the peak of the absorption spectrum in a polar solvent compared to a nonpolar solvent. The details of these measurements have been discussed by Kumar[7] and Liptay[8]. Table I shows the estimated values of hyperpolarizability for the azomethine NLO chromophores.

Table I: Estimated molecular hyperpolarizabilities from solvatochromic data.

MATERIAL	λ_{max} cm^{-1}	ϵ_{max} $M^{-1}cm^{-1}$	μ_g D	μ_{nm} D	$\Delta\omega$ cm^{-1}	$\Delta\mu_{eg}$ D	$\beta_{1.06\mu}$ (X 10^{-30} esu)	$\beta_{1.91\mu}$
M1	27115	36216	5.68	7.89	1134	13.99	101.0	56.5
M2	24950	12425	2.50	5.32	1415	18.49	88.2	41.5
M5	26652	14082	3.81	5.53	1002	8.80	33.9	18.9

λ_{max} = absorption maximum

ϵ_{max} = molar absorptivity coefficient at λ_{max}

μ_g = ground state dipole moment (estimated by molecular mechanics method)

μ_{nm} = transition dipole moment

$\Delta\mu_{eg}$ = $\mu_e - \mu_g$ = change in dipole moment on excitation

$\Delta\omega$ = solvatochromic shift in frequency

The polymers synthesized were also characterized for their molecular weight and their molecular weight distribution using gel-permeation chromatography[4]. As mentioned earlier, the copolymers have high molecular weights compared to homopolymers. Thermal properties such as glass transition temperature and product degradation temperature were determined by differential scanning calorimetry and thermogravimetry methods. The data for different polymers is summarized in Table II.

Table II: Weight- and number-average molecular weights $\overline{M}_w$ and $\overline{M}_n$, $\overline{M}_w/\overline{M}_n$ glass transition temperature Tg and *p*roduct *d*ecomposition *t*emperature PDT of homo- copolymers.

Polymer	$\bar{M}_w$ [a]	$\bar{M}_n$ [a]	$\bar{M}_w/\bar{M}_n$ [a]	T_g in °C [b]	PDT in °C [c]
1c	5 000	1 540	3,3	66	240
2c	4 400	1 670	2,6	52	285
4a	17 700	3 500	5,0	78	275
4b	86 700	40 500	2,1	89	266
3c	1 181 000	195 000	6,1	—	350

[a] Molecular weight was determined by gel-permeation chromatography. Measurements were done in THF using polystyrene standard as reference.

[b] T_g was determined by differential scanning calorimetry (DSC).

[c] Product decomposition temperature (PDT) was determined from thermogravimetry curve.

In addition to the NLO chromophores synthesized, a number of commercially available NLO chromophores were used to make guest-host polymer systems. The commercially available NLO dyes used were 2-methyl-4-nitroaniline (MNA), disperse Red-1 (DR-1) and 4,4-methylene bis(3-nitroaniline) (MBNA). Polymethyl methacrylate (PMMA), Polystyrene (PS) and styrene acrylonitrile copolymer were used as hosts. Figure 5 shows the structure of these NLO dyes and host polymers.

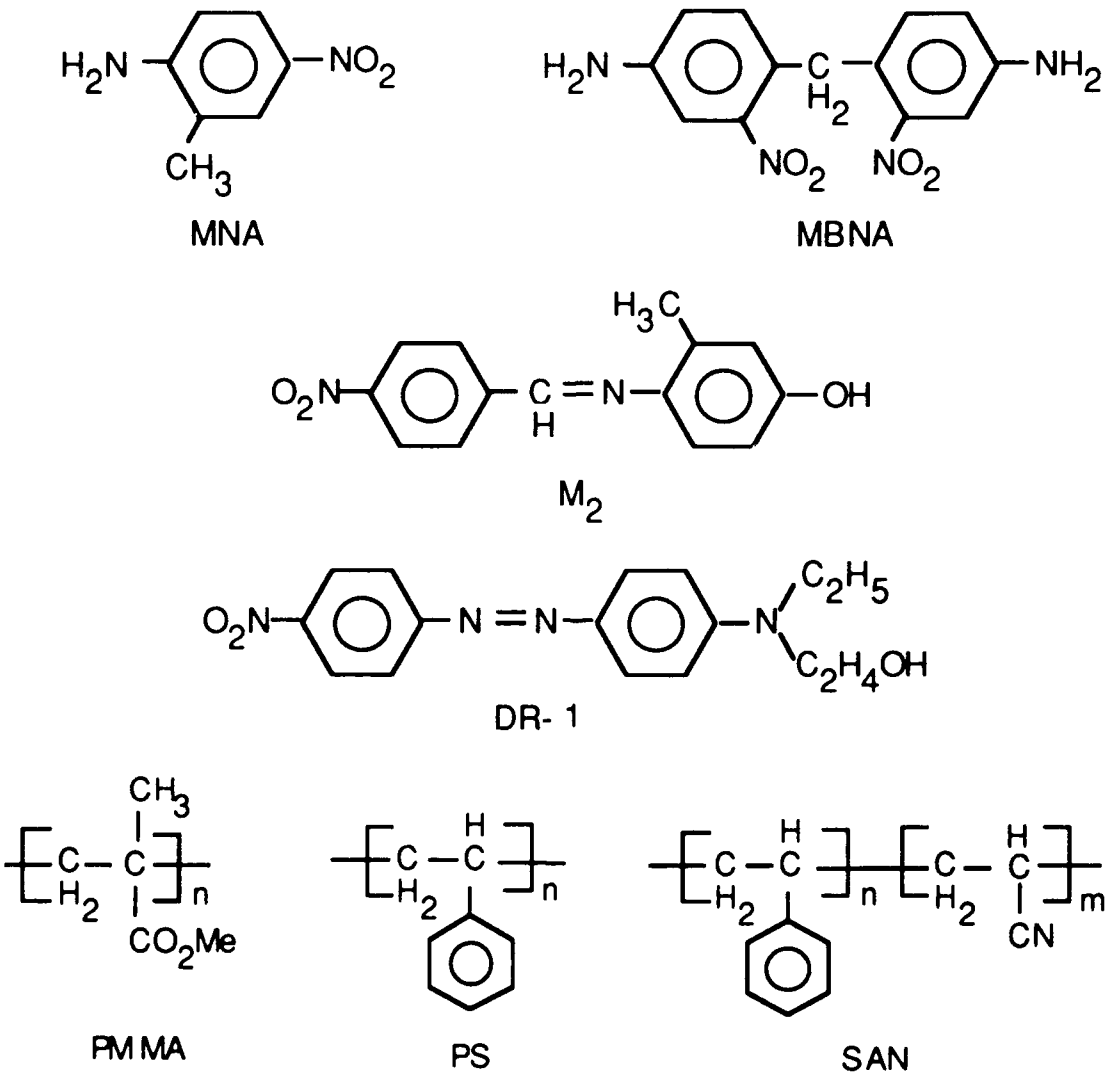


Figure 5. Structures of Selected Guest Molecules and Host Polymers.

The conventional spinning technique employed in microfabrication was employed for coating glass slides or suitable substrates. The polymer and the

NLO chromophore are co-dissolved in a common solvent (for example, 2 gm. of polymer and 0.1 gm. of NLO dye in 10 ml. of N,N-dimethylformamide (DMF)). The resulting solution was filtered and used to spin-coat films between 500-5000 rpm. Film thicknesses ranging from 0.3 to 2.0 microns could be obtained depending on the viscosity and spinning speed. The sample was then baked at 60 °C for for 4 hours in a vacuum oven to remove the trapped solvent. The details of these procedures are discussed by Mandal[9] et al.

Langmuir Blodgett mono and multilayers of some of the NLO dyes modified with appropriate surfactive groups were assembled on a Lauda film balance. Good monolayer forming characteristics are observed when mixed monolayers of the modified M_2 compound are assembled. Monolayers of a number of these compounds have been assembled and reported by Kumar[10] et al. Figures 6 (a) and 6(b) show the pressure area isotherms of mixed monolayers of $HOOC\text{-}(CH_2)_8\text{-}C \equiv C\text{-}C\equiv C\text{-}(CH_2)_8\text{-}CO_2M_2$(compound I) and $CH_3\text{-}(CH_2)_8\text{-}C\equiv C\equiv C\text{-}(CH_2)_{11}\text{-}CO_2M_2$ (compound III). The monolayers yield a high degree of orientation of the dye and consequently a large nonlinear coefficient. However, the enormous time required for assembling many multilayers and scattering from the domains make them very unattractive for integrated optical applications.

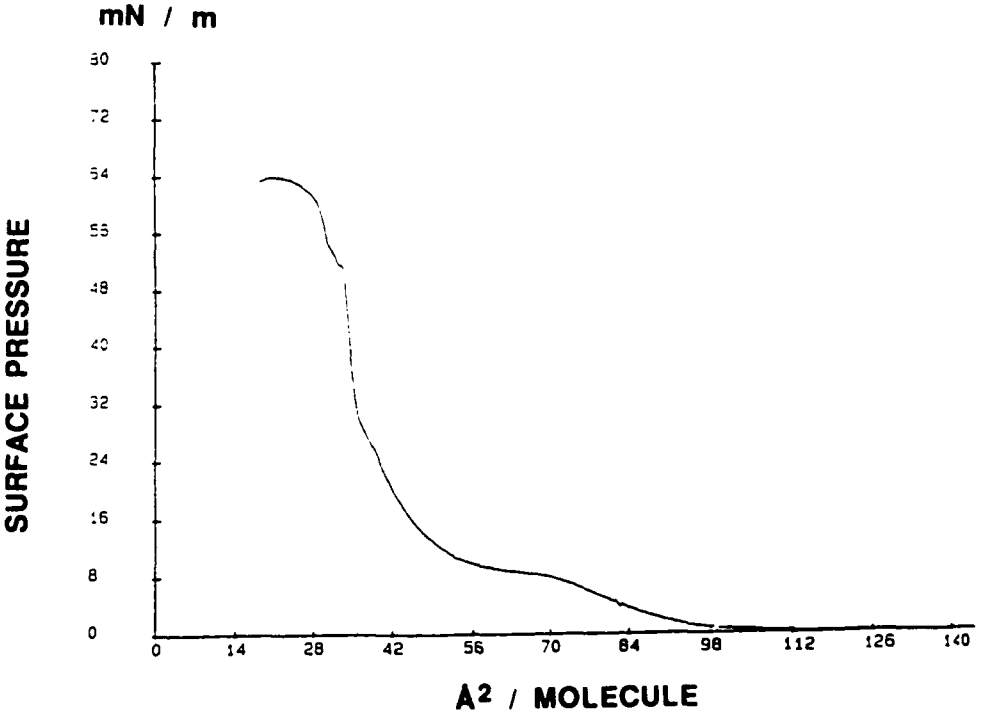


Figure 6a. Mixed Monolayer of Compound I with Stearic Acid.

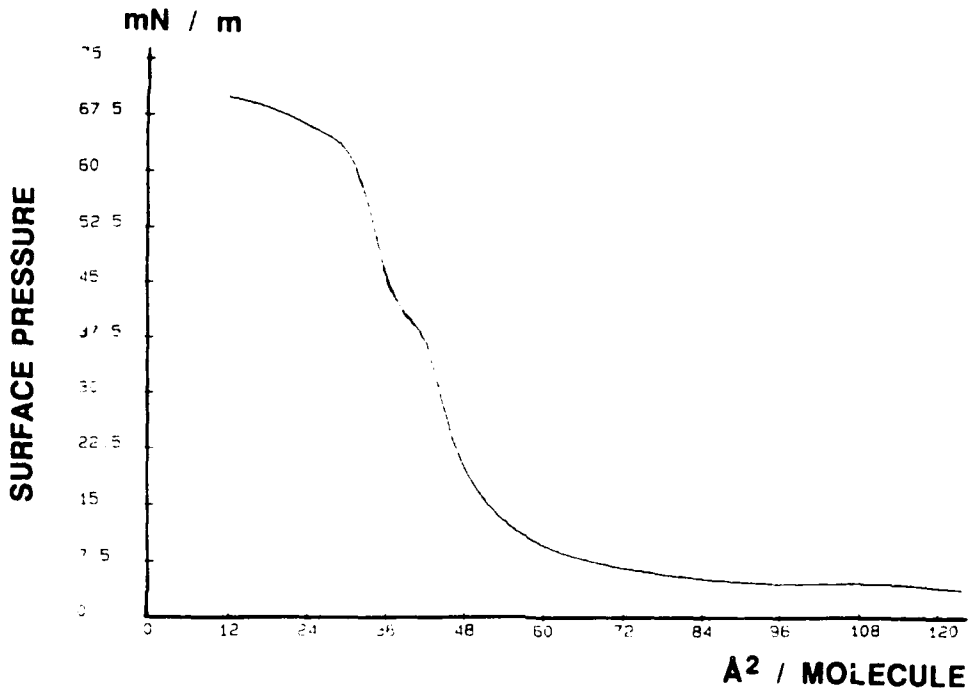


Figure 6b. Mixed Monolayer of Compound III with nonacosa-10, 12-diynoic acid.

To impart second order nonlinearity to the polymer the NLO molecules must be arranged in a noncentrosymmetric structure within the host. This is carried out by applying an external electric field at temperatures near the glass transition temperature (T_g) of the matrix. The active moieties are subsequently "frozen" in the poled phase by cooling the matrix below its T_g while the electric field is still left on. The poling operation can be achieved by electrode poling or corona poling. A corona discharge is partial ionization of air, usually at atmospheric pressure. During the corona poling process, charges deposit on the polymeric film when the applied voltage is higher than the corona discharge voltage. These charges give rise to a large local field given by $E=\sigma/\varepsilon$ where σ is the surface charge density and ε the dielectric permittivity. Figure 7 schematically shows a corona poling arrangement in the wire to plane geometry. The tungsten wire lies in a plane parallel to the plane of the substrate. The value of poling field obtained by corona poling is much higher compared to the parallel plate electrode poling[10].

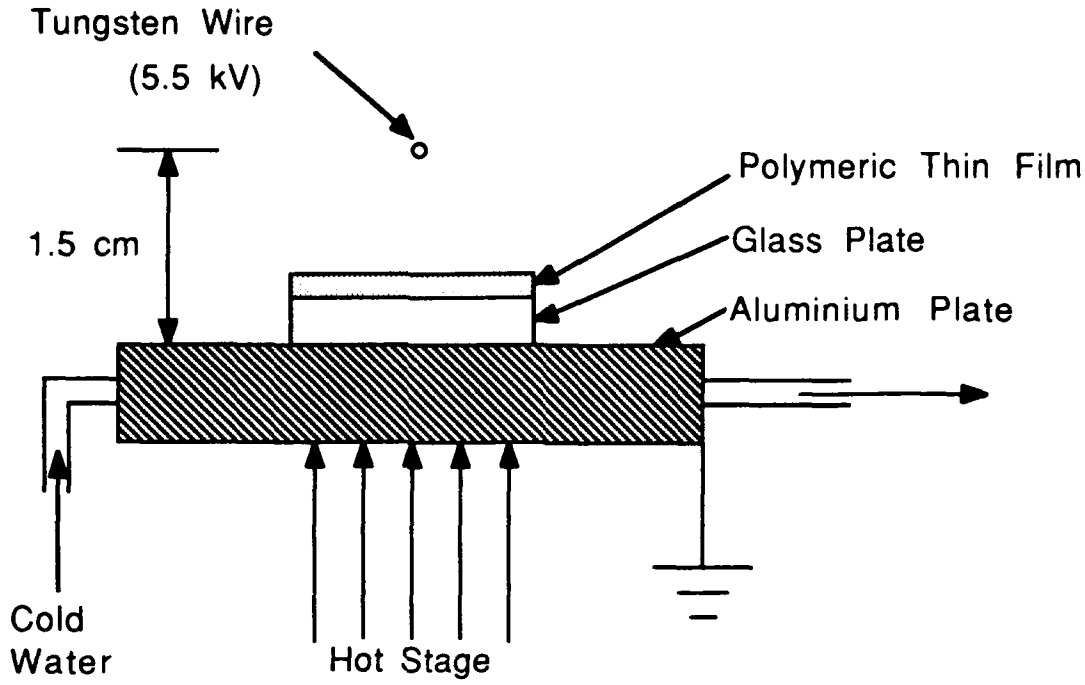


Figure 7. Schematic of a Corona Poling Apparatus.

The principal disadvantage of poled polymer films is the decay in second order nonlinearity with time due to the relaxation of active moieties in the polymer matrix. Grafted systems show slower initial decay compared to guest-host systems at room temperature, but are unstable at higher temperatures. Increasing the glass transition temperature of the polymer invariably leads to better stability at room temperature. Crosslinked polymeric systems usually possess higher glass transition temperatures and are suitable candidates for stable second order nonlinearity.

4. Measurement of linear and nonlinear optical properties.

4.1 Linear Optical Properties

Linear optical properties are extremely important in characterizing a material and also for any practical device design. Optical absorption in thin polymeric films was measured using a Perkin-Elmer Lambda-9 UV-Visible-NIR spectrophotometer. Linear absorption can also be used to monitor decay of alignment of NLO chromophore in a poled polymer. In addition to the losses, the

fringing effect in the transmission spectra can provide a fair idea of the polymer film thickness.

Ellipsometry is also a widely used technique for the measurement of real and imaginary parts of refractive index if the film thickness is known. In the nonabsorbing regime, ellipsometry can be also used to obtain the refractive index and the thickness of the polymer films if the substrate refractive index is known. The accuracy of the measurements is usually determined by the quality of the films. However, in most cases, index can be determined to the second decimal place with accuracy. The ellipsometric measurements were carried out on a Rudolph Research Ellipsometer capable of operation from 0.4 microns to 1.7 microns. The refractive index measurements are crucial for determination of second order nonlinearity. In cases where films are of good enough quality to permit waveguiding in slab geometry, the coupling angles for TE and TM modes permit an accurate determination of index and thickness.

4.2 Second Harmonic Measurements

The NLO coefficient, d_{33}, of the polymers can be obtained by SHG measurements. The detailed calculations of the NLO coefficient, d_{33}, follow Jerphagnon and Kurtz's method. For uniaxial polymeric films, SHG power is generally given by the following equation[11].

$$P_{2\omega} = \frac{8}{\varepsilon_0 A}\, t_\omega^4\, T_{2\omega}\, d^2\, p^2\, P_\omega^2\, R(\theta) \left[\frac{\sin^2\varphi(\theta)}{(n_\omega^2 - n_{2\omega}^2)} \right]$$

A is the area of the laser beam spot, P_ω is the incident laser power, t_ω and $T_{2\omega}$ are the Fresnel-like transmission factors. The n's are the refractive indices at the indicated frequencies, $R(\theta)$ is the multiple reflection correction, and $\varphi(\theta)$ is the angular dependence of the second harmonic power resulting from interference between free and bound waves.

A widely used technique for the measurement of the second order nonlinear susceptibility is one that compares SHG intensity of the unknown sample with a reference material like d_{11} coefficient of fused quartz (Y cut). The peak of second harmonic signal from quartz occurred at normal incidence since the incident beam is p-polarized and parallel to x-axis. Second harmonic intensity

of the polymeric films relative to the reference material (quartz), neglecting multiple reflections[11] is as follows.

$$P_{2\omega} = \frac{8}{\varepsilon_0 A}\, t_\omega^4\, T_{2\omega}\, d^2\, p^2\, P_\omega^2\, R(\theta) \left[\frac{\sin^2\varphi(\theta)}{(n_\omega^2 - n_{2\omega}^2)} \right]$$

$$\frac{P_{2\omega}^s}{P_{2\omega}^q} = \frac{d_s^2\, (t_\omega^4)s\, (T_{2\omega})_s\, R_s(0)\, (n_\omega^2 - n_{2\omega}^2)_q^2 \sin^2\varphi_s p_s^2}{d_q^2\, (t_\omega^4)q\, (T_{2\omega})_q\, R_q(0)\, (n_\omega^2 - n_\omega^2)_s^2 \sin^2\varphi_q p_q^2}$$

d_s And d_q are second harmonic coefficients of the polymeric film and quartz, respectively, and p's are projection factors. Kleinman symmetry (i.e. $d_{31} = d_{15}$) is used here, and d_{33}/d_{31} is assumed to be approximately 3. Figure 8 shows the experimental arrangement for measuring the second order nonlinear susceptibility.

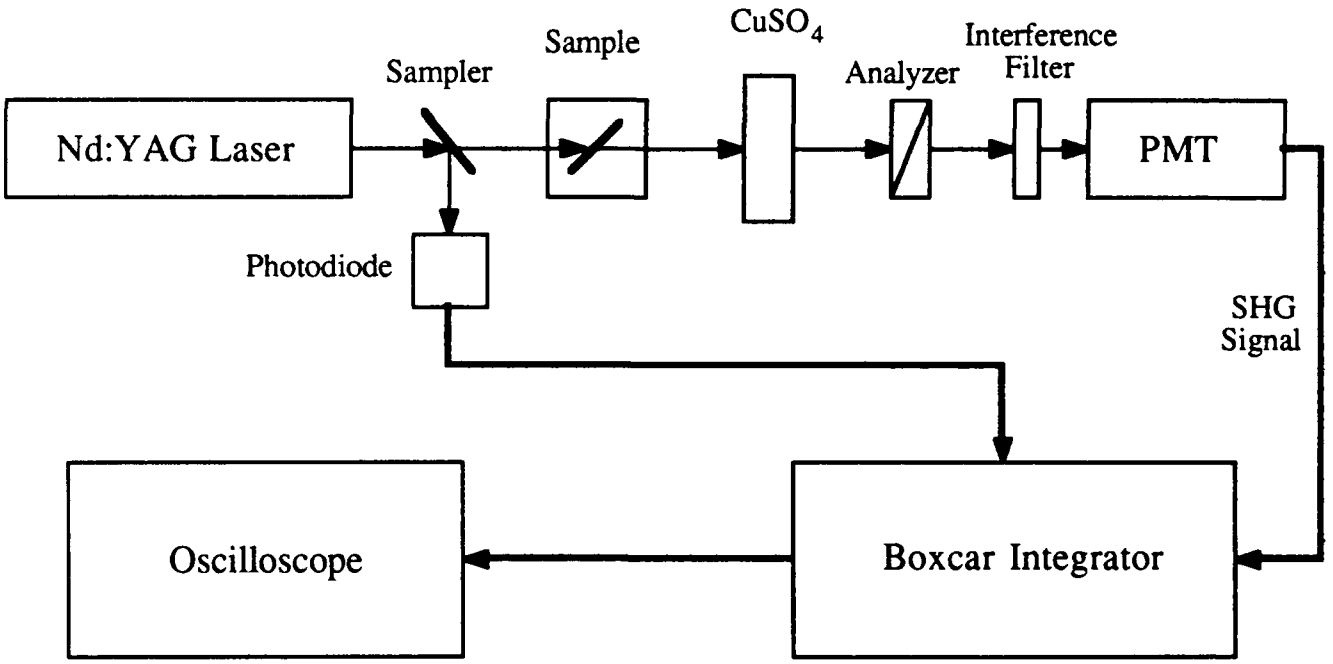


Figure 8. Experimental Set-up for Measuring Second Order Susceptibility.

4.3. Results

Measurements were first done on guest host systems to evaluate their second harmonic response and the temporal stability of the second order nonlinearity. Guest host systems consisting of different NLO dyes in a variety of polymer hosts were investigated. The polymer hosts chosen were PMMA, polystyrene (PS) and SAN. The NLO dyes chosen were MNA, DR-1, M_2, and MBNA. Most guest host systems suffer from the limitation that only a relatively small concentration of dye can be incorporated into the polymer. Concentrations larger than 20 wt. % result in phase segregation and formation of dye crystallites. The dye DR-1 in SAN yielded the largest value of d_{33} of 15pm/V at a concentration of 10 wt. %. The other dyes, due to smaller values of the hyperpolarizability, yielded d_{33} values between 1 and 4 pm/V. The NLO dye M_2 yielded d_{33} = 4pm/V at a concentration of 10 wt %. M_2 has an absorption maxima at a shorter wavelength than DR-1 and is therefore more suitable for applications in the visible. The linear and nonlinear optical properties of the polymers synthesized were measured. The polymer whose structure is shown in Figure 9 is a copolymer of MMA and 4-[4-(-methylacryloxy) octyloxy 2-methylphenyliminomethyl] cyanobenzene (hence referred to as copolymer **1**). The d_{33} for copolymer **1** is found to be about 3 pm/V. This is a large value given the relatively low concentration of the NLO molecules. An improvement of the d_{33} value can be achieved by loading high concentration of NLO molecules.

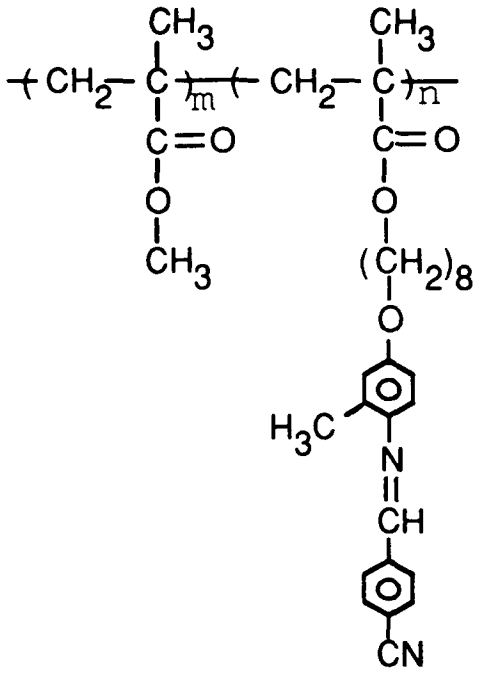


Figure 9. Structure of Copolymer 1.

The temporal stability of the second order nonlinearity is just as important as the magnitude of the nonlinearity. *Unfortunately, at room temperature* the second order nonlinear susceptibility of guest-host polymers decays with time. This decay makes it impossible to utilize guest host systems in practical devices even if the nonlinearity is large. The temporal behavior of second harmonic generation for a number of guest host polymer systems was measured[9]. Figure 10 (a) and (b) show the decay of second harmonic from MNA and DR-1 in different polymer hosts. Intuitively one would expect DR-1 to relax more slowly than MNA because DR-1 is a much larger molecule. However, the relaxation rates seem to depend very much on the dye and the host. This is also illustrated in Figure 11 which shows relaxation of different dyes in the SAN polymer host. Again it is seen that M_2 a larger molecule than MNA, relaxes faster than MNA after poling. The data suggests that the polymer dye interaction may play an important role in determining the relaxation rate.

The aligned active molecules, however, suffer from thermal relaxation when the poling field is removed. The rate of relaxation of orientational order and hence second order nonlinearity in this system largely depends on the polymers, viz. mobility, polarity and interchain free volume [12-15], and the size

and the polarity of the NLO molecules themselves. The decay of the second harmonic intensity from the copolymer **1** was investigated[16] and is shown in Figure 12. The decay of SH coefficient of the copolymer was found to be slower than for guest host systems. This is due to the fact that NLO molecules are linked covalently (grafted) to the side chains of a polymer with polymethylmethacrylate (PMMA) backbone. The movement of NLO molecules are more restricted in this case compared to a guest-host system.

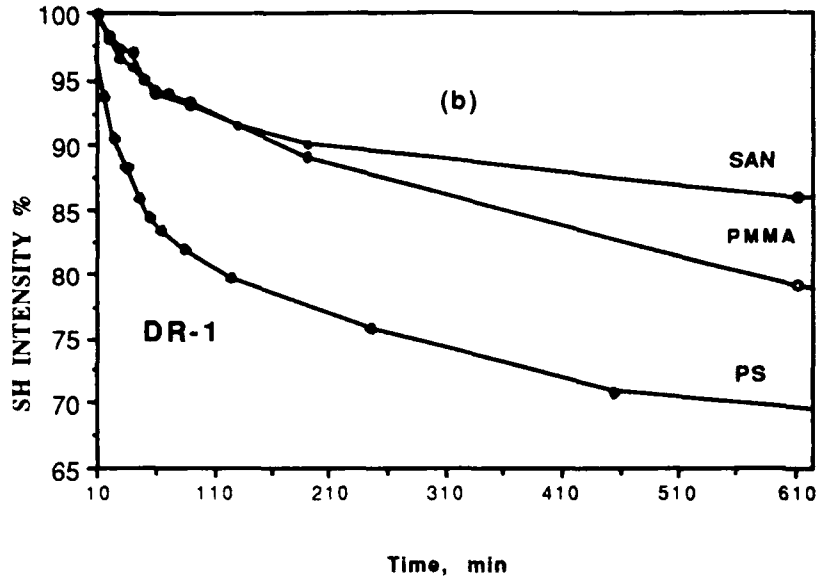


Figure 10a. Decay of Second Harmonic Intensity for MNA in Different Host Polymers.

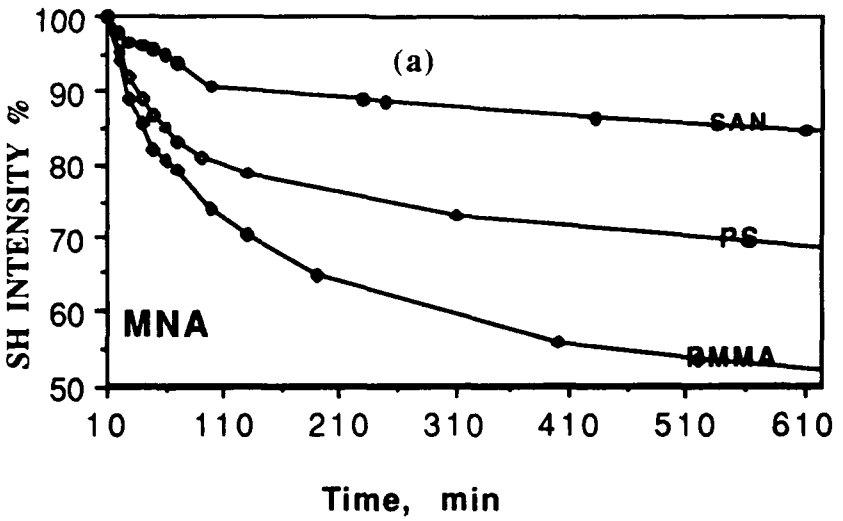


Figure 10b. Decay of Second Harmonic Intensity for DR-1 in Different Host Polymers.

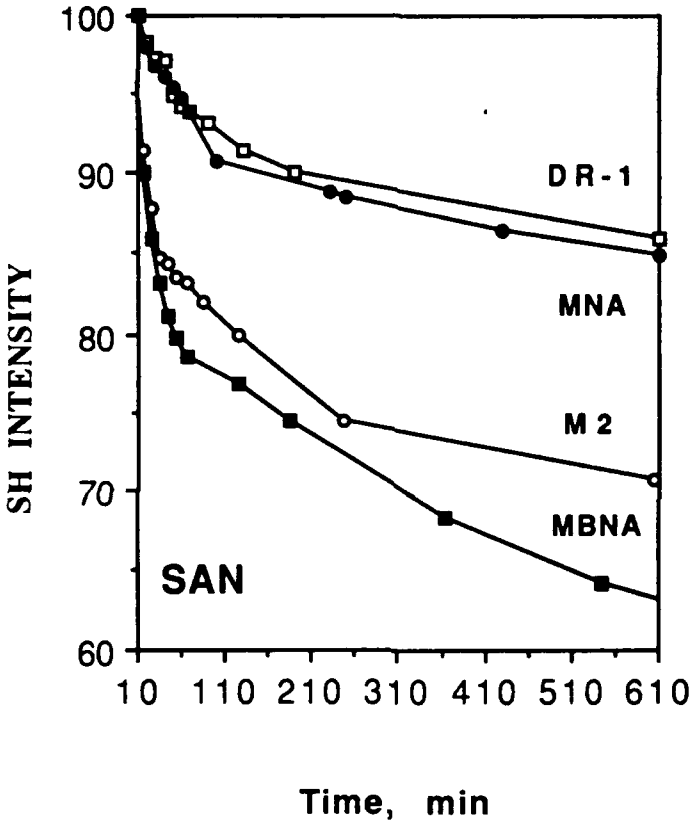


Figure 11. Decay of Second Harmonic Signal of Different NLO Chromophores in SAN.

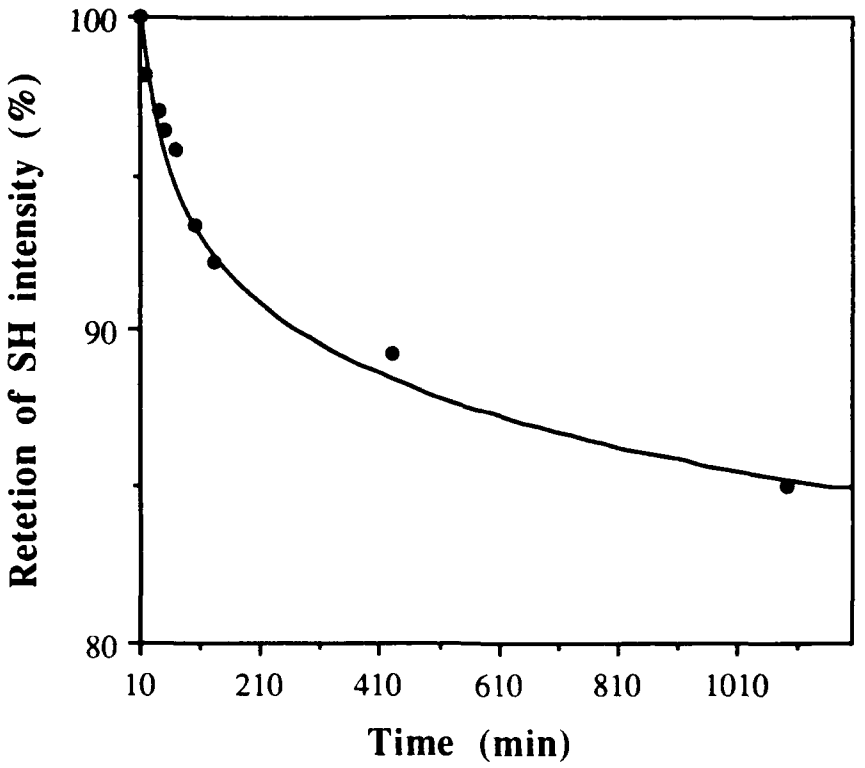


Figure 12. Decay of Second Harmonic in Copolymer 1.

Recently a new guest-host system based on the azo dye disperse red 1 and phenyl siloxane oligomers has been investigated[17] at UMass-Lowell. The second order susceptibility of the polymer cured at 220° C was found to be stable at room temperature and decays to 60 % of its original value (Figure 13) after being maintained at a temperature of 100° C for nearly 30 hours. The linear and second-order nonlinear optical (NLO) properties of this material have been measured and values of second order nonlinearity comparable to other poled polymer systems is achievable. Curing at higher temperatures is expected to lead to greater stability of NLO properties at elevated temperatures. The only limitation to attaining stable second order NLO properties in such a system is the degradation of the NLO chromophore itself. The decay of d_{33} to 60 % of its original value after 30 hours at 100° C is slower than most sidechain or thermally crosslinked NLO polymers. Curing at 300° C or higher can further improve the stability at elevated temperatures. However, an NLO chromophore that is stable at the curing temperature must be used.

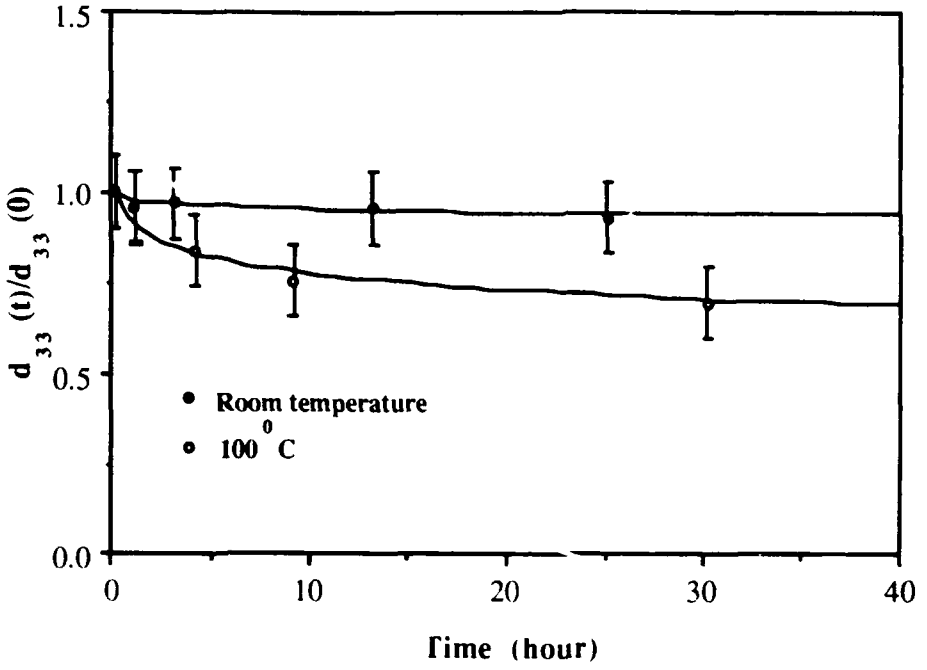


Figure 13. Decay of Second Harmonic Signal in Poled and Cured Phenyl Siloxane with DR-1.

The principal disadvantage of this type of poled films is the decay in second order parameters with time, due to the relaxation of active moieties in the polymer matrix, especially for guest-host systems. Grafted systems show slower initial and long term decay of second order NLO properties at room temperature, but are unstable at higher temperatures. Increasing the glass transition temperature of the polymer invariably leads to better stability at room temperature. Crosslinked polymeric systems usually possess higher glass transition temperatures and therefore, are suitable candidates for stable second order nonlinearity.

A Michelson interferometer is utilized for measuring the linear electro-optic coefficient (Pockels' coefficient) of thin film samples. Figure 14 schematically shows the experimental arrangement of the Michelson interferometric technique. For this configuration, sample preparation is simple and effects of air currents, vibrations, and temperature fluctuations are much smaller than those for a Mach-Zender interferometer. The sample is placed in one of the arms of the interferometer and a modulating electric field is applied to the sample.

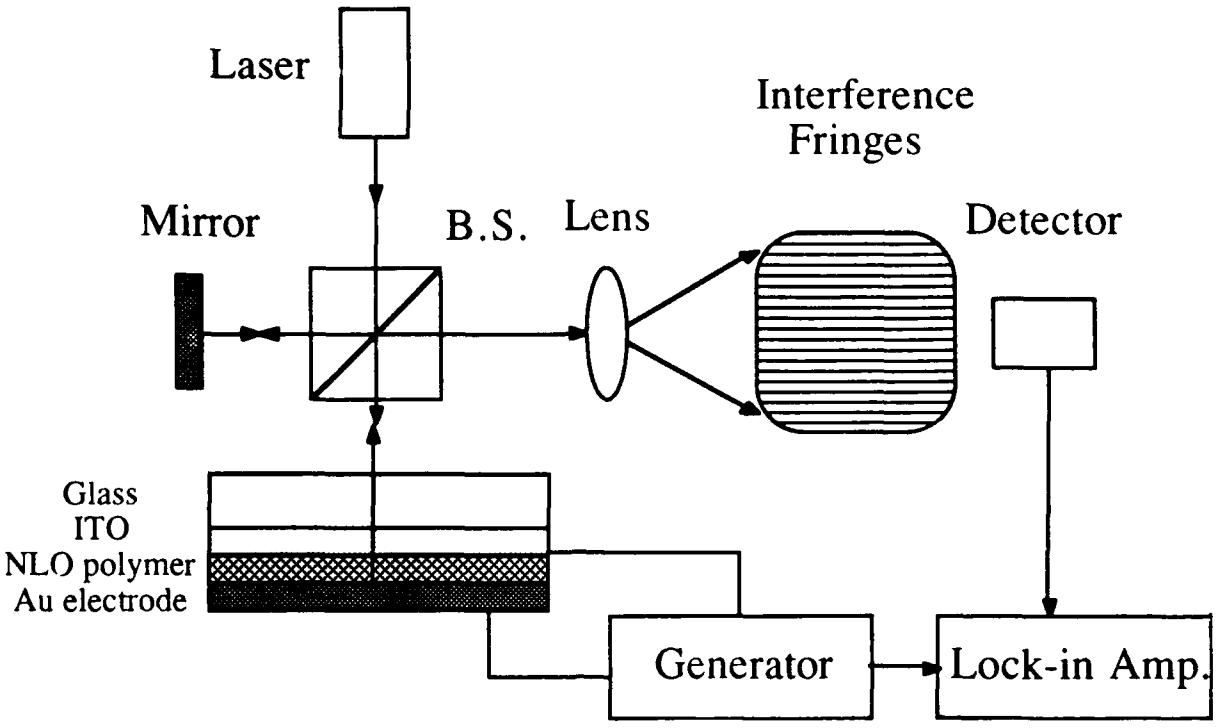


Figure 14. Michelson Interferometer for Measurement of Electro-optic Coefficient.

In the sample arm of the interferometer, a laser beam propagates through an indium-tin-oxide (ITO) coated glass substrate, a thin NLO polymer film, and is then reflected back by a metal electrode. The intensity of a fringe pattern is given by:

$$I(\phi) = I_r + I_s + 2\sqrt{I_r I_s}\cos\phi$$

where I_r and I_s are the intensities of the beams in the reference and sample arms respectively, and ϕ is the phase difference between the two beams. The change in the intensity due to a small change in the phase difference is therefore given by:

$$\Delta I = -2\sqrt{I_r I_s}\sin\phi\Delta\phi = \frac{I_{max} - I_{min}}{2}\sin\phi\Delta\phi$$

where $I_{max}=I(0)$ and $I_{min}=I(\pi)$ are the maximum and minimum intensities. ϕ is biased at either $\pi/2$ or $-\pi/2$ where ΔI is linearly proportional to $\Delta\phi$. To set

the bias, a translation stage is used to adjust the position of the slit detector so that the intensity is at $(I_{max} + I_{min})/2 = I(\pi/2) = I(-\pi/2)$. For a film with a thickness, d, and a linear EO coefficient, r_{13}, and a modulating voltage, $V = V_m \cos\Omega t$,

$$\Delta\phi = \frac{2\pi}{\lambda} 2d\Delta n = - \frac{2\pi n^3 r_{13} V_m}{\lambda} \cos \Omega t$$

where λ is the wavelength of light. At the bias points $\phi = \pi/2$ or $-\pi/2$

$$\Delta\phi = \frac{(I_{max} - I_{min})\pi n^3 r_{13} V_m}{\lambda} = - \cos \Omega t \equiv I \overset{+}{\Omega} \cos \Omega t$$

Measurement of the amplitude of the modulated interferometer output allows the measurement of the electrooptic coefficient, r_{13}. The coefficient, r_{13}, of the guest host polymers and the sidechain polymers range from 1 to 5 pm/V. The r_{33} coefficient is approximately three times r_{13} which makes the polymers practical for electro-optic modulation although the halfwave voltages are still higher than the ferroelectrics like lithium niobate. However, the lower dielectric constants make them very attractive for high speed applications.

4.4. Third Order Nonlinear Optical Properties

An interferometric technique, similar to the one discussed above, can be used to evaluate the quadratic electro-optic coefficient, which is related to the third order nonlinear susceptibility, $\chi^{(3)}$. In this case the quadratic electro-optic (E-O) coefficient, S_{1133}, is given by:

$$S_{1133} = (1/\pi n^3) [(I_{2\omega+} - I_{2\omega-})/(I_{max} - I_{min})] (\lambda d / V_m^2)$$

where n is the refractive index, λ is the laser wavelength, d is the thickness of the film, V_m is the modulating voltage at frequency ω, I_{max} and I_{min} are the maximum and minimum intensities of the interference fringe, and $I_{2\omega+}$ and $I_{2\omega-}$ are the modulations at two half-intensity points of a selected interference fringe at frequency 2ω. The modulated intensities occur at a frequency of 2ω because the phase change depends on the square of the modulating field.

The dye incorporated polymers are not only useful as second order NLO materials, but at high dye concentrations have fairly large values of nonresonant third order susceptibilities[18,19]. Of course, poling is not required if only third order properties are desired. The UMass Lowell group, along with some other groups, have recently reported measurements on the third order nonlinearities of these dye incorporated polymeric systems. The measured quadratic E-O coefficient as a function of dye concentration (CNNB/R) is shown in Figure 15. An approximately linear relationship exists between them, which indicates no aggregation in this dye-doped polymer system. The quadratic E-O coefficients in this system are large compared with those of our former systems based on azomethine dyes at the same dye concentrations. These glassy, dye-incorporated polymers also have significant processing advantages over crystalline materials which make them attractive for integrated optics applications such as the nonlinear waveguide coupler.

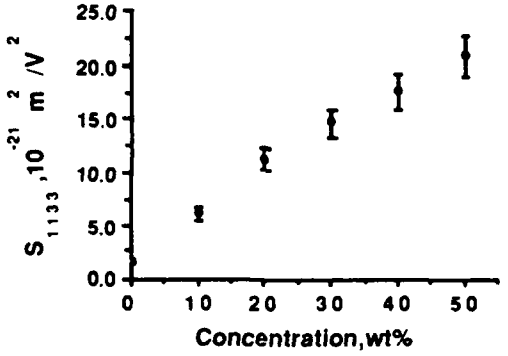


Figure 15. Plot of Quadratic E-O Coefficient Versus the Concentration of the NLO Dye CNNB-R.

The thickness and refractive index of unpoled copolymer **1** were found to be 1.95 μm and 1.525, respectively, for 633 nm wavelength, using the waveguiding technique. No anisotropy between TE polarization and TM polarization was observed in the unpoled sample. Figures 16(a) and 16(b) show the reflected intensity vs. external angle of incidence for TE_0 and TE_1 modes, respectively. Figures 17(a) and 17(b) show the reflected intensity vs. external angle of incidence for TM_0 and TM_1 modes, respectively. There are minima in the reflected intensity for both TE or TM polarization. The well resolved minima attest to the excellent optical quality of the film. The refractive indices of the

poled sample, determined using waveguiding technique, were found to be 1.523 for TE polarization and 1.534 for TM polarization at wavelength 633 nm. The poled sample showed a birefringence of 0.011. The refractive index and thickness of the film were also measured using an ellipsometer and found to be in excellent agreement with those obtained by the prism-coupling technique. The thickness of the film were also determined from its UV-Visible transmission spectra on fused quartz substrate, taking the refractive index of the film to be 1.525. The value of the thickness obtained from UV-Visible transmission spectra agrees with that obtained by the prism-coupling technique within 6% error.

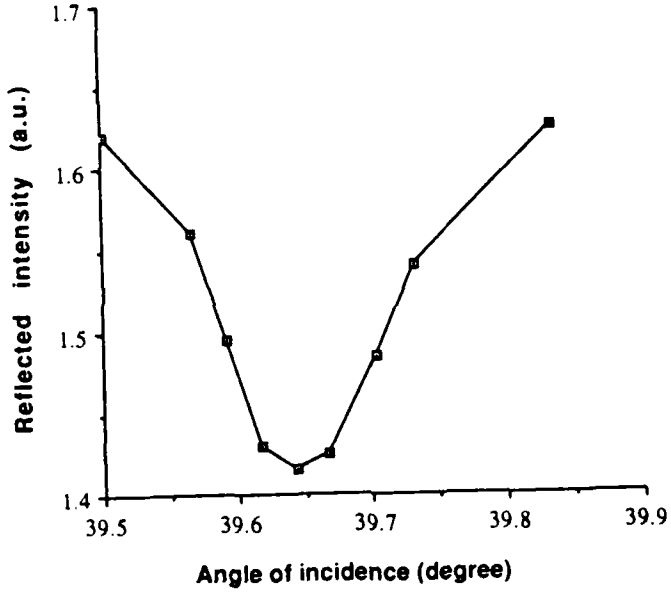


Figure 16a. Reflected Intensity vs. External Angle of Incidence for TE_0 Mode.

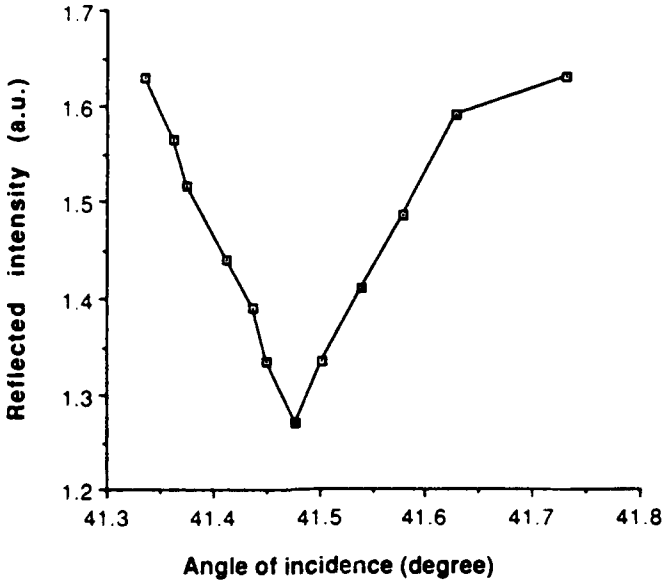


Figure 16b. Reflected Intensity vs. External Angle of Incidence for TE_1 Mode.

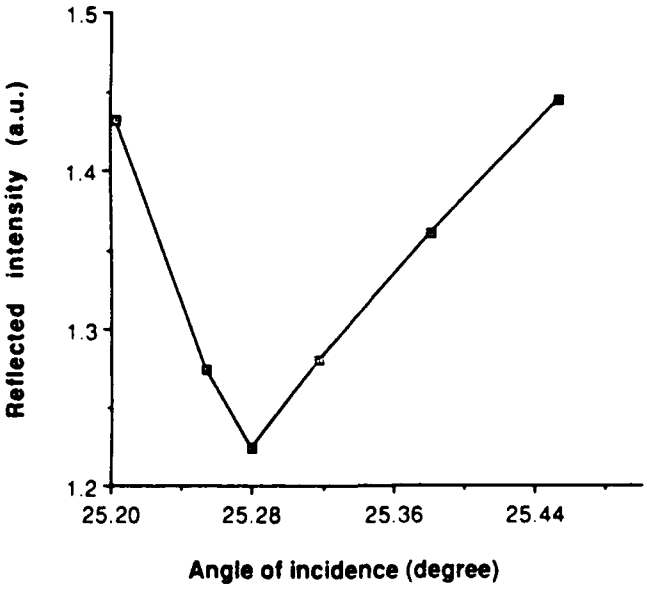


Figure 17a. Reflected Intensity vs. External Angle of Incidence for TM_0 Mode.

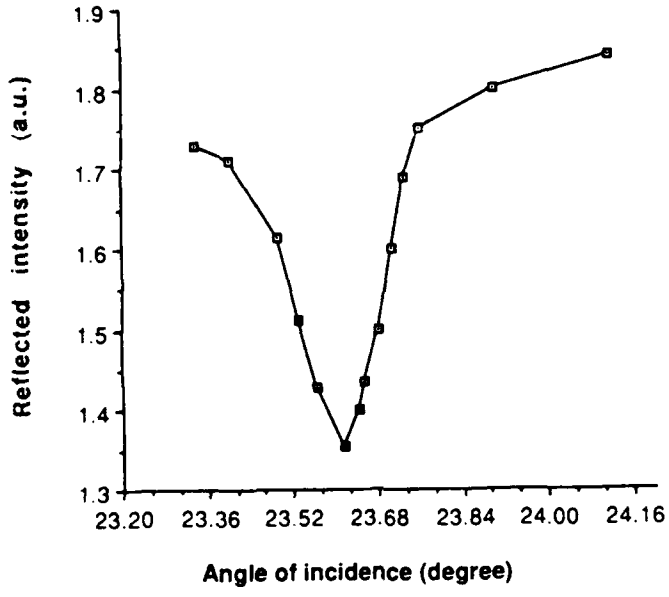


Figure 17b. Reflected Intensity vs. External Angle of Incidence for TM_1 Mode.

The loss was determined by using the assumption $I = I_0 \exp(-ax)$ [21], where I is the intensity scattered from the waveguide at any point, x along the waveguide streak, I_0 is the intensity at x=0, and α is the attenuation coefficient. A plot of ln(I) vs. x for copolymer **1** is shown in Figure 18. The waveguide loss was found to be 1 dB/cm at 633nm wavelength. The absorption loss at this wavelength is negligible so that losses are mostly due to scattering. Preliminary measurements on second harmonic generation in polymer waveguides indicate that efficiencies of the order of 1% may be feasible with a coupled fundamental power of 100 mW.

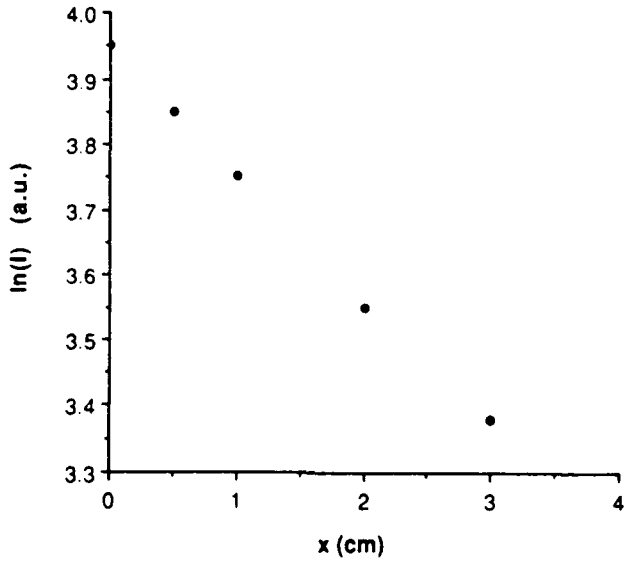


Figure 18. Plot of In (I) vs. x for Copolymer 1.

Conclusions

A number of polymeric second and third order nonlinear optical materials were designed and synthesized. The materials were characterized for their thermal properties and processed into thin films by Langmuir-Blodgett technique or spin coating methods. Linear optical properties of the materials were measured by UV-Visible spectroscopy and ellipsometry. The second and third order nonlinear optical properties of the polymeric materials were evaluated by second harmonic generation and electric field induced phase changes by interferometry. Stable second order nonlinear coefficient was obtained in crosslinked systems. Waveguiding with low loss was achieved in spin coated nonlinear optical polymer films and frequency doubling experiments in waveguide configuration were performed.

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